Hydrothermal transformation of porous glass granules into ZSM-5 granules

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Abstract

A direct synthesis of ZSM-5 granules from the hydrothermal treatment of porous glass granules, in the presence of monopropylamine, at 175 °C, is reported. The course of the transformation of porous glass granules into ZSM-5 granules has been investigated using X-ray diffraction (XRD), infrared spectroscopy (IR), 11B and 27Al MAS–NMR spectroscopy, scanning electron microscopy (SEM), N2-adsorption and mercury porosimetry measurements. Inductively coupled plasma-emission (ICP) spectrometry has been used to monitor the role played by various species (Si, B, Al and Na) during the initial stages of the transformation process. The characterization results reveal that the ZSM-5 granules obtained from porous glass granules possess a combination of macropores (porous glass matrix) and micropores (ZSM-5). Thus, a binder-free zeolite ZSM-5 with a bimodal pore structure has been successfully synthesized.

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1. Introduction

In the past few years, a great deal of attention has been paid to zeolite coatings on various macroporous supports [1,2]. Such composite materials could provide easier access of the reactants to the active sites and also avoid mass transport limitations. Several porous materials, such as glass [3], Al2O3 [4], stainless-steel [5–7], ceramic foam [8,9], cordierite honeycomb [10] and anion exchange resin beads [11], have been used as supports. Among the supports, porous glass discs and tubes are promising candidates to synthesize zeolite composite membranes [12–14]. These membranes have been shown to selectively permeate N2 compared to O2. In addition, attempts have also been made to transform porous glass into various zeolites such as ZSM-5 [15–19], Ferrierite [19], Silicalite-1 [20,21] and Theta-1 [22]. Recently, we have reported the transformation of porous glass beads into ZSM-5 beads without changing their original size and shape [23]. This method offers a promising alternative to conventional approaches for the preparation of binderless preshaped zeolites. Such preshaped zeolites possess microporous and macroporous characteristics of zeolite and porous glass, respectively. Thus, these hybrid (porous glass–zeolite) materials are expected to exhibit improved performance in separations and catalysis.

Furthermore, there has been considerable work on the preparation of preshaped zeolites [24–27]. A preshaped crystalline aluminosilicate ZSM-5 has been synthesized by crystallizing a preformed reaction mixture...
containing clay, sodium silicate and tetrapropylammonium hydroxide [24]. The hydrothermal transformation of amorphous aluminum silicate pellets into ZSM-5 pellets using TPABr as the template has been reported by Weisser et al. [25]. The preparation of ZSM-5 zeolite film on silica extrudates has been described by Danner and Unger [26]. In addition, the synthesis of zeolite ZSM-5 on a porous granulated silica gel support has also been reported by Landau et al. [27]. In this paper, we report our systematic studies on the hydrothermal transformation of porous glass granules into ZSM-5 granules using monopropylamine as the template. In addition, the course of the transformation process has been followed by different characterization techniques (XRD, IR, 11B MAS–NMR, SEM, N2 adsorption and Hg porosity measurements).

2. Experimental

2.1. Materials

TRISOPOR® porous glass granules with an average pore size of 32nm were obtained from VitraBiO GmbH. The particle diameter of the porous glass granules was in the range of 315–500μm. The chemical composition (wt.%) of the porous glass granules was 88% SiO2, 0.6% Na2O, 0.09% Al2O3, 5.6% B2O3, 5.0% H2O. Monopropylamine (98%), aluminum sulfate [Al2(\(\text{SO}_4\))\text{3} \cdot 16\text{H}_2\text{O}, 51–59%] and sodium hydroxide (NaOH, 99%) were purchased from Merck.

2.2. Hydrothermal transformation of porous glass granules into ZSM-5 granules

In a typical procedure, monopropylamine (PA) was added into an aluminum [Al2(\(\text{SO}_4\))\text{3} \cdot 16\text{H}_2\text{O}] containing alkaline (NaOH) solution. Then, the porous glass granules were suspended in the above mixture. The over-all composition of the reaction mixture, expressed in mole ratios of the oxides, was as follows: 9Na2O:4B2O3:1Al2O3:72SiO2:117PA:2726H2O. The resultant mixture was degassed for 20 min before transferring into a stainless-steel autoclave (55ml). The transformation of porous glass granules into ZSM-5 granules was carried out under rotation (~20rpm) conditions by placing the autoclave on the rotating shaft in a preheated convection oven at 175°C. After the desired period of time, the autoclave was removed from the oven and quenched in cold water. The products were collected by filtration, washed thoroughly with deionized water and dried at 100°C for 16h.

2.3. Characterization

X-ray diffraction patterns were obtained on a URD 63 Seifert X-ray diffractometer with Ni-filtered monochromatic CuKα radiation. The XRD measurements were carried out in the range 2θ of 3–40° at a scan rate of 0.05°min\(^{-1}\). The crystallinity parameter (\(Q_{\text{Al}}\)) was calculated on the basis of a method reported previously [23]. Infrared (IR) spectra were obtained using the KBr pellet technique in a Perkin–Elmer infrared spectrometer in the range of 400–2000cm\(^{-1}\). 11B MAS–NMR measurements were carried out on a Bruker spectrometer at a Larmor frequency of 96.3MHz and a rotation frequency of 4kHz. The N2 adsorption measurements were carried out using a Sorptomatic 1900 (Carlo Erba Instruments) and the surface area was calculated using the Dubinin method. Mercury porosimetry measurements were carried out using a porosimeter 4000 (Carlo Erba Instruments). The chemical composition of the samples was determined by inductively coupled plasma-emission (ICP, Perkin–Elmer 400). Prior to the ICP analysis, the samples were dissolved by micro-wave heating in an aqueous HF solution.

3. Results and discussion

3.1. X-ray diffraction and chemical analysis

Fig. 1 shows the evolution of XRD patterns of the ZSM-5 phase from porous glass granules at 175°C as a function of time. The XRD pattern of the starting porous glass granules (curve ‘a’) shows a broad halo in the 2θ range of 17–27°, suggesting its amorphous nature. The samples collected even after a period of 12 and 24h (curves ‘b’, and ‘c’) are amorphous according to

![Fig. 1. X-ray powder diffraction patterns of: (a) the starting porous glass granules and the product samples withdrawn at different intervals of transformation of porous glass granules into ZSM-5 granules at 175°C (b) 12h, (c) 24h, (d) 36h (e) 49h, (f) 55h, (g) 61h and (h) 72h [9Na2O:4B2O3:1Al2O3:72SiO2:117PA:2726H2O].](image-url)
However, the shape of the amorphous halo changed considerably indicating that the process of transformation of porous glass granules was already in progress. The characteristic reflections corresponding to ZSM-5 phase ($\theta = 5.9^\circ$ and $23^\circ$) start appearing after $36\text{h}$ (curve ‘d’); thereafter as the time progresses the intensity of the ZSM-5 reflections increases gradually (curves ‘e’, ‘f’ and ‘g’). The XRD pattern of the sample collected after $72\text{h}$ (curve ‘h’) matches well with the reported XRD pattern of the ZSM-5 structure [28]. No impurity phases were detected. The absence of amorphous background and the high intensity of the peaks, indicate that the ZSM-5 phase obtained from porous glass granules is phase-pure and highly crystalline. A plot of the crystallinity parameter ($Q_{\text{Al}}$) versus time is shown in Fig. 2. In general, the nucleation and crystal growth processes of zeolites are described by sigmoid curves [29]. However, it is evident from Fig. 2 that the induction period is significantly longer (0–24h), thus indicating that the ZSM-5 granules were obtained by slow crystallization from porous glass granules. The overall crystallization process of ZSM-5 granules from porous glass granules can be divided into three stages: (i) an induction period (0–24h), (ii) an initial period of slow crystallization (24–50h) and (iii) a much faster crystal growth period (50–72h).

In order to get a better insight into the process of transformation of porous glass granules into ZSM-5 granules, both filtrate and solid samples were collected from the synthesis mixture over a period of 6h and analyzed by ICP. It can be seen from Fig. 3 that a small amount of Si was found in the filtrate only after a period of 30min which reached saturation within 1h. The observation of Si, along with the detection of B in the filtrate samples, indicates the partial dissolution of porous glass granules during the hydrothermal transformation. No Al was detected in the filtrate collected after a period of 1h, indicating its adsorption or complexation onto the surface of the porous glass granules. It is worthy to note that after 1h, a steady-state composition is reached in the filtrate. The chemical analysis reveals that the amounts of dissolved Si and B in the filtrate sample collected after 6h are 4 and 14 (wt.%), respectively. The chemical compositions of the solid samples collected from the synthesis mixture over a period of 6h are shown in Fig. 4. It was found that the SiO$_2$/Al$_2$O$_3$ ratio decreased from 320 (0h) to 70 (1h) and remained constant over a period of 6h, indicating complete adsorption or complexation of Al onto the surface of the porous glass granules. At the beginning, the dissolution of B occurred and no further significant change in the SiO$_2$/B$_2$O$_3$ ratio was observed after 1h. It is also evident that the Na$_2$O/SiO$_2$ ratio increased from 0.015 (0h) to 0.075 (6h) indicating the role of Na as a counter cation. From the above results, we can conclude that the...
transformation of porous glass granules into ZSM-5 granules involves three steps: (i) partial dissolution of porous glass granules up to the saturation of silicon in the solution phase, (ii) adsorption or complexation of Al onto the surface of porous glass granules and (iii) total transformation of amorphous porous glass granules into crystalline ZSM-5 granules.

3.2. Infrared spectroscopy

The course of transformation of porous glass granules into ZSM-5 granules was also followed by IR. The IR spectrum of porous glass granules (curve ‘a’ in Fig. 5) exhibits three bands at 1400, 922 and 678 cm\(^{-1}\) [30]; these bands are characteristic of threefold coordinated B species. In addition, porous glass granules display a band at 1102 cm\(^{-1}\); which is attributed to the tetrahedral coordinated Si, Al and B-atoms. The intensity of the bands assigned to the threefold coordinated boron species gradually decreases (curves ‘b’, ‘c’, ‘d’ and ‘e’) during the transformation of porous glass granules into ZSM-5 granules. Note that the IR spectra of the samples collected after 24 and 36 h (curves ‘f’ and ‘g’) reveal the absence of threefold coordinated B species. Furthermore, the bands (1222, 555 and 450 cm\(^{-1}\)) characteristic of pentasil zeolites [31] are clearly seen in the IR spectrum of the sample collected after 72 h (curve ‘h’). The high intensities of the bands at 555 cm\(^{-1}\) and 450 cm\(^{-1}\) indicate that the ZSM-5 granules obtained from porous glass granules are highly crystalline.

3.3. \(^{11}\)B and \(^{27}\)Al MAS–NMR spectroscopy

In order to probe the local environment of B and Al atoms, \(^{11}\)B and \(^{27}\)Al MAS–NMR measurements were carried out on the starting porous glass granules and the samples collected during the transformation of porous glass granules into ZSM-5 granules. The \(^{11}\)B MAS–NMR spectrum (curve ‘a’ in Fig. 6) of the porous glass granules is composed of a powder pattern exhibiting two peaks at 5.0 and \(-14.0\) ppm and a strong signal at \(-1.6\) ppm. The two peaks at 5.0 and \(-14.0\) ppm are typical for a second-order quadrupole powder pattern in the case of axial symmetry of the electric field gradient and are ascribed to threefold coordinated B species [30]. The strong signal (\(-1.6\) ppm) is related to the presence of tetrahedral coordinated B in amorphous porous glass granules. It can be seen that the peaks assigned to threefold coordinated B disappeared completely after 12 h (curve ‘b’). This result substantiates the solubility of threefold coordinated B species and the presence of only tetrahedral B species in the amorphous matrix during the transformation of porous glass granules into ZSM-5 granules in agreement with the IR spectroscopic results. Furthermore, it was found that with increasing crystallization time [36 h (curve ‘c’), 49 h (curve ‘d’),

![Fig. 5. IR spectra of: (a) the starting porous glass granules and the product samples withdrawn at different intervals of transformation of porous glass granules into ZSM-5 granules at 175°C; (b) 10 min; (c) 30 min; (d) 60 min; (e) 2 h; (f) 24 h; (g) 36 h and (h) 72 h.](image1)

![Fig. 6. \(^{11}\)B MAS-NMR spectra of: (a) the starting porous glass granules and the product samples withdrawn at different intervals of transformation of porous glass granules into ZSM-5 granules at 175°C; (b) 12 h; (c) 36 h; (d) 49 h; (e) 55 h; (f) 61 h and (g) 72 h.](image2)
55h (curve ‘e’) and 61h (curve ‘f’), the intensity of the peak (−1.6 ppm) assigned to tetrahedral coordinated B in amorphous porous glass granules decreased and the intensity of the peak (−2.6 ppm) assigned to tetrahedral coordinated B in ZSM-5 granules increased simultaneously. From the chemical analysis, it was found that the amount of B in the partially and fully crystalline products remains the same indicating the complete transformation of tetrahedral coordinated B in amorphous surroundings into tetrahedral coordinated B in the ZSM-5 granules. It is interesting to note that the $^{11}$B MAS–NMR spectrum of the sample collected after 72h (curve ‘g’) is less complex, showing only the presence of B in tetrahedral coordination in ZSM-5 granules along with trace amount of tetrahedral B in amorphous surroundings. No broad signal exhibiting peaks at −14.0 and 5.0 ppm could be observed. This confirms that there are no threefold coordinated B species in the ZSM-5 granules. The number of B atoms per unit cell (u.c.) was found to be 3 for the fully crystalline ZSM-5 granules with a SiO$_2$/B$_2$O$_3$ ratio of 60. This value is marginally lower than the upper limit reported for the MFI structure (4 B/u.c.) [32].

The $^{27}$Al MAS–NMR spectra of the samples collected during the transformation of porous glass granules into ZSM-5 granules are shown in Fig. 7. Interestingly, the sample collected after 12h (curve ‘a’), which is amorphous according to XRD, shows a single line at 56 ppm assigned to the tetrahedral Al species. This confirms that Al species present in the solution phase are rapidly adsorbed or complexed onto the surface of the porous glass granules. Most interestingly, the sample collected after 72h (curve ‘b’) shows a much sharper signal than that of the sample collected after 12h. This suggests the better crystallinity of ZSM-5 granules in comparison to the sample collected after 12h. Similar observations have been reported earlier on the synthesis of zeolite A (Na-form) [33]. No signal is observed below 50 ppm. This confirms that there is no extra-framework Al species (penta- or hexa-coordinated) in the ZSM-5 granules.

### 3.4. Scanning electron microscopy (SEM)

Scanning electron micrographs were taken, in order to show that the shape of the starting porous glass granules remains intact during their transformation into ZSM-5 granules. A SEM image of the starting porous

![Fig. 8. SEM images of: (a) the starting porous glass granules; (b) the surface of a starting porous glass granule; (c) ZSM-5 granules obtained from porous glass granules (72h) and (d) the surface of a ZSM-5 granule.](image-url)
glass granules with their typical irregular shape is shown in Fig. 8a. In addition, a high magnification SEM image (Fig. 8b) reveals a rough surface texture of the porous glass granules. Though not evident in this figure, the pore size of the porous glass granules was estimated to be 32 nm by mercury porosimetry analysis. A SEM image of the fully crystalline ZSM-5 granules (Fig. 8c) reveals that the physical shape of the starting porous glass granules is preserved during the hydrothermal synthesis process and nearly free from the powders of zeolite ZSM-5. It is pertinent to mention here that the particle diameters (315–500 μm) are the same for both the fully crystalline ZSM-5 granules and the starting porous glass granules. Interestingly, a high magnification image (Fig. 8d) shows that the outer surface of the granules is completely covered by ZSM-5 crystals. It can be seen that the majority of the ZSM-5 crystals are cuboid and rectangular in shape and are in the range of 100–200 nm. These observations lead to the conclusion that the crystallization took place in the matrix of the porous glass granules.

### 3.5. Micro- and macroporosity

The textural properties of the starting porous glass granules and the synthesis products collected after different crystallization times were determined by N\textsubscript{2} adsorption and mercury porosimetry methods. The results are summarized in Table 1. Note that the specific surface areas of the samples were calculated from the N\textsubscript{2} adsorption isotherms using the Dubinin method [34]. The specific surface area and the micropore volume of the porous glass granules are 108 m\textsuperscript{2} g\textsuperscript{-1} and 0.007 cm\textsuperscript{3} g\textsuperscript{-1}, respectively. The sample collected after 24 h has a low surface area (65 m\textsuperscript{2} g\textsuperscript{-1}), indicating that the pores of porous glass granules are either narrowed or blocked by dissolved Si species, thereby reducing the internal surface area available for N\textsubscript{2} adsorption. It can be seen, from the data shown in Table 1, that there is a significant increase in the surface area (from 65 to 333 m\textsuperscript{2} g\textsuperscript{-1}) with an increase in crystallization time (from 24 to 72 h). Such a progressive increase in the surface area correlates with the formation of micropores in the macroporous glass matrix. The surface area (333 m\textsuperscript{2} g\textsuperscript{-1}) and the pore volume (0.11 cm\textsuperscript{3} g\textsuperscript{-1}) obtained for the highly crystalline ZSM-5 granules are marginally lower than the values reported for the MFI structure [35]. The N\textsubscript{2} adsorption isotherms illustrated in Fig. 9 show distinct textural differences between the starting porous glass granules and the synthesis products collected after different crystallization times. The porous glass granules (curve ‘a’) exhibit a type II isotherm [36] because of their macroporous nature. The samples collected after 24, 49, 61 and 72 h (curves ‘b’, ‘c’, ‘d’ and ‘e’) show a gradual increase in the uptake of N\textsubscript{2} in the P/P\textsubscript{0} region of 0–0.01.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N\textsubscript{2} adsorption</th>
<th>Hg-porosimetry</th>
<th>Total porosity ((\epsilon))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface area (m\textsuperscript{2} g\textsuperscript{-1})</td>
<td>Micropore volume (cm\textsuperscript{3} g\textsuperscript{-1})</td>
<td>Macropore volume (cm\textsuperscript{3} g\textsuperscript{-1})</td>
</tr>
<tr>
<td>Porous glass granules(d)</td>
<td>108</td>
<td>0.007</td>
<td>1.266</td>
</tr>
<tr>
<td>24 h(e)</td>
<td>65</td>
<td>0.002</td>
<td>0.923</td>
</tr>
<tr>
<td>36 h</td>
<td>72</td>
<td>0.009</td>
<td>0.933</td>
</tr>
<tr>
<td>48 h</td>
<td>89</td>
<td>0.017</td>
<td>0.970</td>
</tr>
<tr>
<td>61 h</td>
<td>209</td>
<td>0.063</td>
<td>0.861</td>
</tr>
<tr>
<td>72 h</td>
<td>333</td>
<td>0.110</td>
<td>0.808</td>
</tr>
</tbody>
</table>

\(a\) Dubinin method.  
\(b\) t-plot method.  
\(c\) \(\epsilon = \frac{v_{\text{Macro}} + v_{\text{Meso}} + v_{\text{Micro}}}{\frac{Q}{H}}\).  
\(d\) Starting porous glass granules.  
\(e\) Sample collected after 24 h.
Also the isotherm (type II) exhibited for porous glass granules disappears gradually. The $\text{N}_2$ adsorption of the highly crystalline ZSM-5 granules (curve ‘e’) exhibits a type I isotherm [36], which is characteristic of microporous materials. The macropore volume estimated from mercury porosimetry measurements is also reported in Table 1. For the starting porous glass granules, the macropore volume was 1.266 cm$^3$/g. Upon increasing the crystallization time, the macropore volume decreased from 1.266 to 0.808 cm$^3$/g. However, it can be seen from Table 1 that there is little difference between the total porosity values observed for the starting porous glass granules (0.74) and the highly crystalline ZSM-5 granules (0.67). This suggests that the ZSM-5 granules obtained from porous glass granules possess both the micro- and macroporous characteristics.

4. Conclusions

In conclusion, a binder-free zeolite ZSM-5 with a bimodal (micro–macro) porosity has been synthesized by hydrothermal treatment of porous glass granules, in the presence of monopropylamine, at 175 °C. The course of transformation of porous glass granules into ZSM-5 granules was followed by various physico-chemical characterization techniques. XRD patterns show the gradual transformation of amorphous porous glass granules into highly crystalline ZSM-5 granules. The results of ICP analysis of the filtrate and the solid samples collected from the synthesis mixture suggest that transformation of porous glass granules into ZSM-5 granules occurs in three stages: (i) partial dissolution of porous glass granules up to the saturation of silicon in the solution phase, (ii) adsorption or complexation of Al onto the surface of porous glass granules and (iii) total transformation of amorphous porous glass granules into crystalline ZSM-5 granules. The formation of a five-membered ring of the ZSM-5 structure is indicated in the framework IR spectra of the samples. $^{11}$B and $^{27}$Al MAS–NMR studies indicate the presence of Al and B atoms in tetrahedral coordinations. SEM images indicate that the physical shape of the starting porous glass granules is preserved during the hydrothermal transformation process. Porosimetry measurements ($\text{N}_2$ adsorption and mercury porosimetry) reveal the micro- and macroporous characteristics of ZSM-5 granules.

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